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REEVALUATION OF PHENYLFLUORONE METHOD OF THE DETERMINATION OF T--ETC(U)
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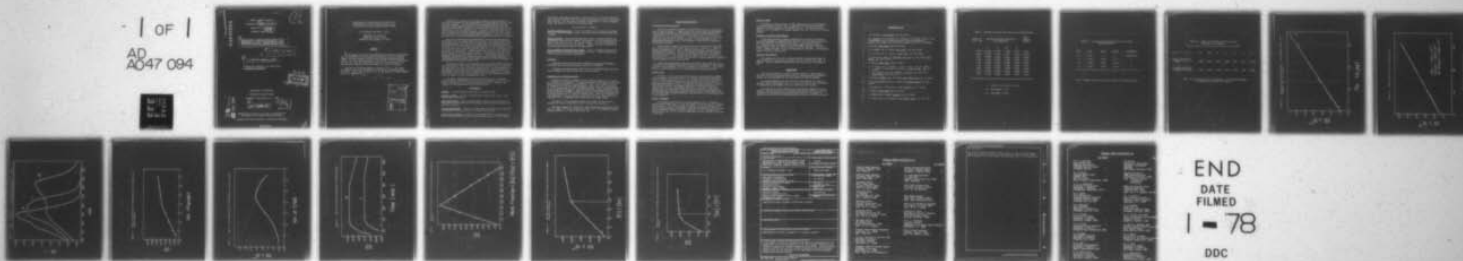
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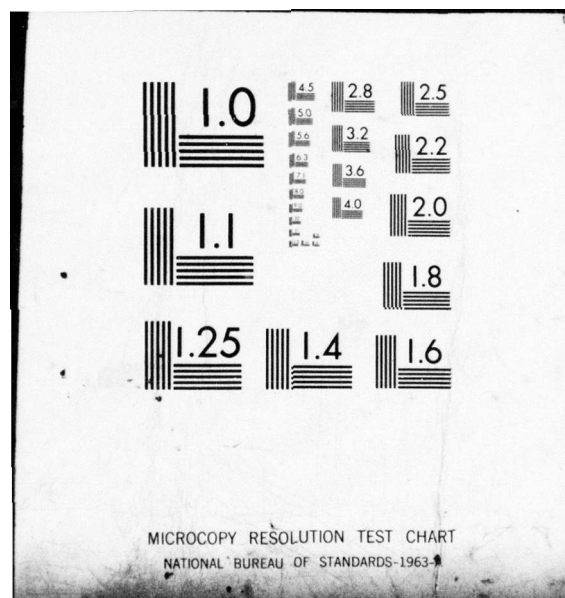
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Office of Naval Research

Contract No. ⁽¹³⁾ N00014-76-C-0836

Project No. NR 356-626

Technical Report No. ^{(14) TR-} 4

⁽²⁾ REEVALUATION OF PHENYLFLUORONE METHOD OF THE
DETERMINATION OF TIN IN SUB-MICROGRAM LEVELS
USING CETYL TRIMETHYL AMMONIUM BROMIDE (CTAB)

by

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Prepared for submission for publication
in Analytical Chemistry.



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⁽¹¹⁾
120 October 20, 1977

⁽¹²⁾ 21 p.

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Reevaluation of Phenylfluorone Method for the
Determination of Tin in Sub-microgram Levels
Using Cetyl Trimethyl Ammonium Bromide (CTAB)

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ABSTRACT

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In an attempt to improve the phenylfluorone method for determining tin, the modification of the visible spectrum of tin (IV) fluorone complex has been studied by adding cetyl trimethyl ammonium bromide (CTAB). The band maximum observed at 530 nm for tin (IV) fluorone complex does not show any bathochromic shift but the absorbance of the band maximum is greatly enhanced compared with previous methods.

The tin (IV) fluorone complex is formed at pH 1.2. The color development takes about 30 minutes and the color is stable for about two hours. Beer's law is obeyed up to 3.0 μg , giving a working range of 0.2 to 3.0 μg Sn/50 ml.

micrograms

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Efforts in our laboratory have been focussed on the improvement of colorimetric methods for the determination of tin leached from marine coatings into seawater. A variety of marine antifouling coatings have been developed using organotin toxicants. The successful coatings have low leach rates and various hydrolysis mechanisms have been postulated for the dissolution of the tin moieties (1,2). In order to determine leach rates and to evaluate the proposed leaching mechanisms one must be able to determine tin accurately in submicrogram range in seawater. Thus, this study was undertaken to evaluate and optimize the fluorone method for tin analysis.

Since the introduction of phenylfluorone for the spectrophotometric estimation of tin in various matrices by Luke(3), many modifications have been suggested for the improvement of sensitivity and reproducibility(4-8). Recently, Smith(9) has reported a modified method for determining tin in the range of 0.3 to 3.0 μg , where he has abandoned the use of gelatin as well as the acetate buffer, and developed the color at pH 1.0. He claims that the method is reproducible. Russian workers have reported that the use of phenylfluorone (Pf) with antipyrine (Ap) in the presence of mineral acid anion (anion) in the molar ratio 1:2:1 viz. Pf:Ap:anion, yields a four component complex which can readily be extracted into chloroform(10). These reactions are reported to be highly sensitive and are recommended for determining microgram quantities of tin.

Sensitizers, such as cetyl trimethyl ammonium bromide (CTAB) and cetylpyridinium bromide (CPyB) have been used with catechol violet to increase the sensitivity of this colorimetric method(11,12). No such attempts have been reported in the case of phenylfluorone method. The success of the sensitizers tried in the case of catechol violet indicated that it should be worthwhile to try one of these sensitizers for the fluorone method and study its impact on the Sn determination limit.

From these investigations it has been found that cetyl trimethyl ammonium bromide (CTAB) does not produce any bathochromic shift in the absorption maximum of tin(IV) fluorone complex at 530 nm. However, the intensity of the band maximum is markedly improved.

EXPERIMENTAL

Reagents. All the reagents used were of analytical grade.

Sulfuric acid(2N): 55.5 ml of concentrated sulfuric acid (Sp.gr. 1.84) were diluted to one liter.

Sodium Acetate(4M): 136 g of sodium acetate trihydrate were dissolved in about 150 ml of distilled water by heating, after cooling the solution was diluted to 250 ml.

Sodium hydroxide(4N): 160.0 g of sodium hydroxide pellets were dissolved in distilled water and diluted to one liter after cooling.

Tin(IV) stock solution: 0.1000 g of pure granulated tin was dissolved in 20 ml of concentrated sulphuric acid by heating to fumes. After cooling,

the solution was added cautiously to about 150 ml of ice-cooled distilled water and an additional 65 ml of concentrated sulphuric acid was introduced with stirring. The solution was cooled, transferred to a liter volumetric flask, and diluted to mark with distilled water.

1 ml of solution = 100 μ g Sn

Tin(IV) standard solution: 1.00 ml of tin(IV) stock solution was diluted to 100 ml, with 2N sulphuric acid. This solution was prepared fresh when required.

Phenyl fluorone: 10 mg of phenylfluorone (Aldrich analyzed sample), was dissolved in about 25 ml of ethanol containing 0.2 ml of concentrated sulphuric acid, and diluted to 100 ml with ethanol. The solution stored in dark is stable for at least two months. 0.0001 M Solution prepared from the stock solution was used for the measurements.

Cetyl trimethyl ammonium bromide (CTAB): 0.10 g of CTAB was dissolved in distilled water by warming, and diluted to 100 ml. 0.0001 M Solution of CTAB was used in the color development.

Apparatus:

A Beckman Zeromatic II pH meter equipped with glass and reference electrodes was used for measuring the pH of the solutions.

A Beckman spectrophotometer model DU with 1 cm matched glass cells was used to measure the optical densities of the solutions.

Preparation of Calibration Graph:

Transfer by pipette, standard tin(IV) solution (from 0.2 to 4.0 μ g) to a series of 50 ml beakers. To each beaker add the following in the order shown, mixing thoroughly at each addition. Add 4.5 ml of CTAB, 20 ml of 2N sulphuric acid and mix them thoroughly. Adjust the pH of the solution to 1.2 by adding drop by drop 4N sodium hydroxide. Add 2 ml phenylfluorone solution and mix thoroughly. Transfer the solutions quantitatively to the 50 ml calibrated volumetric flasks, and dilute to mark with distilled water, having pH adjusted to 1.2 with 2N sulphuric acid. Leave for 40 minutes at room temperature and then measure the optical density of each solution in 1 cm glass cell at wavelength 530 nm with water as reagent blank.

The graph of optical density against the amount of tin in μ g is a straight line over a range from 0.2 to 3.0 μ g of tin (Fig. 1a).

The least squares fit obtained for this calibration graph has an intercept of 1.3664×10^{-2} and a slope of 1.3718×10^{-2} . The computed standard deviation amounts to 7.4261×10^{-3} (Fig. 1b).

RESULTS AND DISCUSSION

The Spectral Characteristics:

The partial absorption spectra of phenylfluorone and its tin(IV) complex are shown in Fig. 2. Phenylfluorone in ethanol shows a broad maximum in the range of 460-480 nm. The aqueous solution of phenylfluorone containing CTAB at pH 1.2 displays an intense band maximum at 460 nm and an inflection in the region 430-440 nm. The absorption at 460 nm is more intense than that noted for ethanol solution. This enhancement in the absorbance is apparently due to the presence of CTAB which is capable of bonding with fluorone.

In the tin(IV) complex, the band at 460 nm is sufficiently suppressed and a high-intensity band maximum appears exactly at 530 nm. We have repeated the experiments of Luke(1), Bennett and Smith(2), and Smith(7) to compare with our results. The optical densities observed at the optimum wavelength and percentage increase in the optical densities observed are given in Table II. It is obvious from the results that in the present work the intensity of the band maximum of the tin(IV) fluorone complex is greatly increased compared with the other methods.

It has been established in the case of catechol violet that the use of CTAB causes a considerable bathochromic shift in the spectrum of the tin(IV) catechol violet complex(11,12) and an increase in absorbance. A much smaller effect has been observed for the lanthanum-xylene orange complex(13).

Effect of pH:

The effect of pH on the Sn determination has been examined by adding various amounts of 4M sodium acetate to a series of solutions containing 2 ml of 0.0001 M solution of tin, 4.5 ml of CTAB, and 20 ml of 2N sulphuric acid. 4 ml of 0.0001 M fluorone is then added to each solution and the solutions are diluted to 50 ml. The optical densities measured at the optimum wavelength reveal that maximum sensitivity is obtained at pH 1.2 (Table III). The use of 4N sodium hydroxide in the place of 4M sodium acetate does not considerably affect the optical densities and hence, in further experiments 4N sodium hydroxide has been used. Measurements above pH 2 have not been attempted because of contribution due to the anionic form of the ligand(14).

Effect of Reagent:

It is evident from the plot of optical density (O.D.) vs volume of phenylfluorone added (Fig. 3), that the excess of fluorone does not decrease the absorbance. The rapid increase is observed in the initial stage, and after 4 ml of fluorone, the increase in the optical density for the next successive addition of phenyl fluorone is gradual. It may, therefore, be concluded that for 0.0 to 2.0 ml of 0.0001 M Sn, 4.0 ml of 0.0001 M fluorone can be used.

Effect of CTAB:

The effect of the variation of CTAB concentration on the absorbance of tin(IV)-fluorone complex (Fig. 4) indicates that maximum absorbance is obtained for CTAB volumes in the range of 4-5 ml. The volume has been fixed at 4.5 ml (0.0001 M) to produce maximum color for the tin(IV) fluorone complex.

Stability of Tin-Fluorone Complex:

It has been reported in Smith's method that two hours are required for the development of complete color and that the color fades at the rate of 1% per hour for the following four hours. In the present method it is observed that the complete color development occurs in about 30 minutes (Fig. 5) and the color is stable for about two hours. After two hours a gradual decrease in the color intensity is observed. This decrease amounts to about 1.14% per hour.

Nature of the Complex:

The composition of tin(IV) fluorone complex in presence of CTAB has been determined by continuous variation (Fig. 6) and mole ratio (Fig. 7) methods. Both the methods indicate that the ratio of tin to fluorone is 1:2.

CONCLUSIONS

The visible spectrum of tin(IV) fluorone complex in the presence of CTAB does not show any bathochromic shift in the band maximum observed at 530 nm, but the absorbance of the band maximum is greatly enhanced.

The method compares very well with the recent method of Corbin(12) and gives the working range of 0.2 to 3.0 μg of tin per 50 ml. The method is reproducible and comparatively more rapid than that of Smith.

The combination of this method with a preliminary separation of tin either by solvent extraction or by distillation should produce a sensitive technique for determining sub-microgram quantities of tin present in various matrices such as antifouling paints, seawaters, and food materials.

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Table I. Calibration Figures Obtained by the Proposed Method.

Amount of Sn in μg	Optical densities observed for four replicates				Mean Optical Density
	I	II	III	IV	
0.20	0.0120	0.0110	0.0100	0.0125	0.0113
0.40	0.0160	0.0160	0.0155	0.0150	0.0156
0.60	0.0190	0.0200	0.0201	0.0210	0.0200
0.80	0.0255	0.0235	0.0230	0.0230	0.0237
1.00	0.0263	0.0270	0.0280	0.0250	0.0265
1.40	0.0370	0.0299	0.0355	0.0300	0.0331
2.00	0.0470	0.0370	0.0450	0.0420	0.0427
2.50	0.0440	0.0520	0.0450	0.0460	0.0467
3.00	0.0640	0.0540	0.0520	0.0520	0.0555

i Volume of the solution = 50 ml

ii Cell Length = 1 cm

iii Wavelength = 530 nm

Table II. The Observed Optical Densities for the Other Reported Methods.

pH	O.D.	Δ O.D	% Δ O.D	References
1.2	0.215	-	-	Present Work
1.0	0.160	0.055	34.77	7
1.8	0.180	0.035	19.44	1
3.5	0.188	0.027	14.36	2

Note: 0.0001M Solution of tin(IV) is taken for the measurements.

Table III. Effect of Variation of pH on the Color Intensity of the Complex.

pH-----	0.5	0.85	1.0	1.2	1.6	1.8	2.0
Optical Densities of Blank-----	0.005	0.013	0.013	0.002	0.021	0.023	0.0235
Optical Densities for 0.0001M Sn Solution--	0.012	0.142	0.163	0.213	0.209	0.207	0.209

Note: The optical densities are measured at the optimum wavelength as shown by the scans of the spectra.

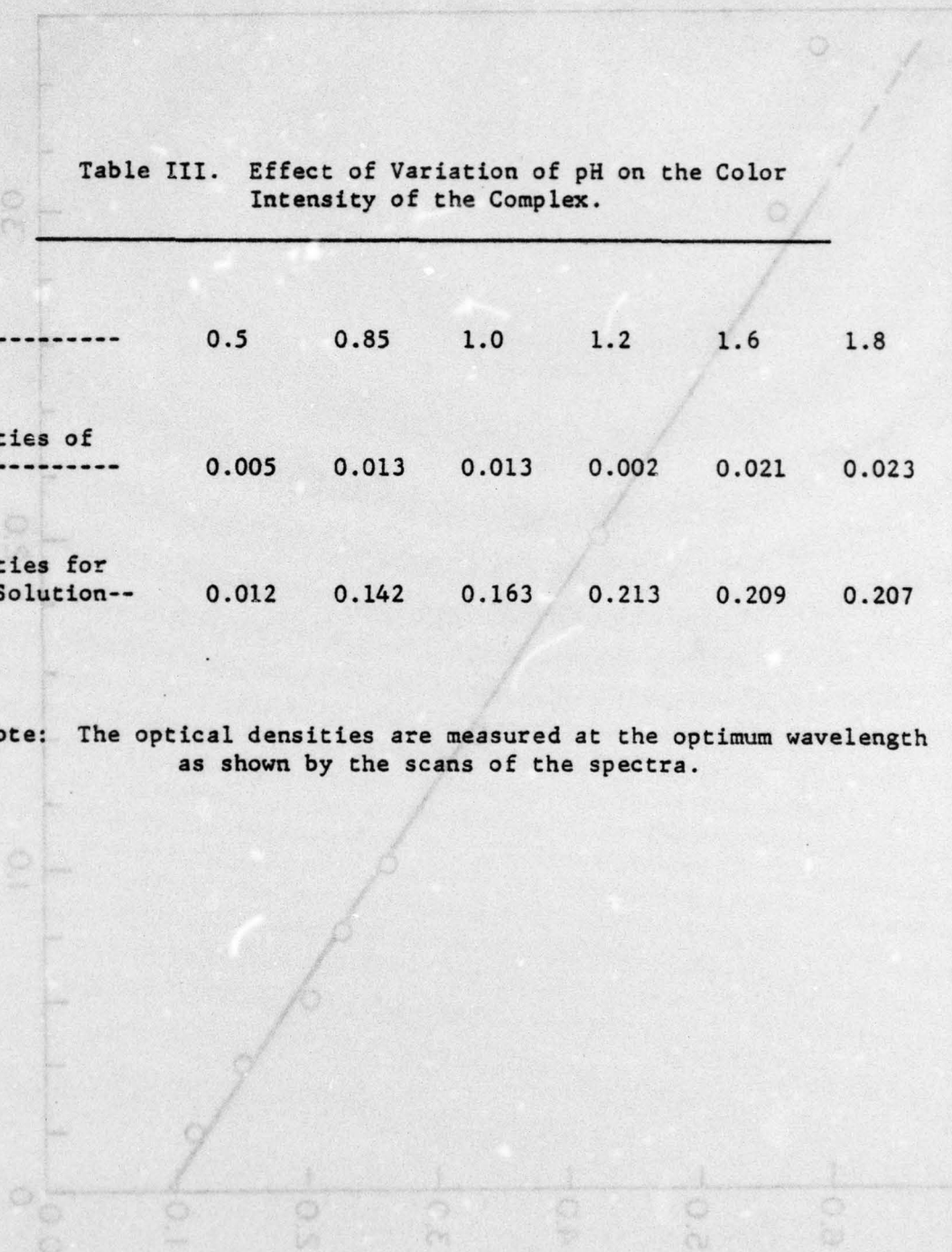


Figure 1a. Beer's Law Curve (Phenylfluorone: 2 ml (0.0001M); CTAB: 4.5 ml (0.0001M); pH: 1.2, 1 cm cell).

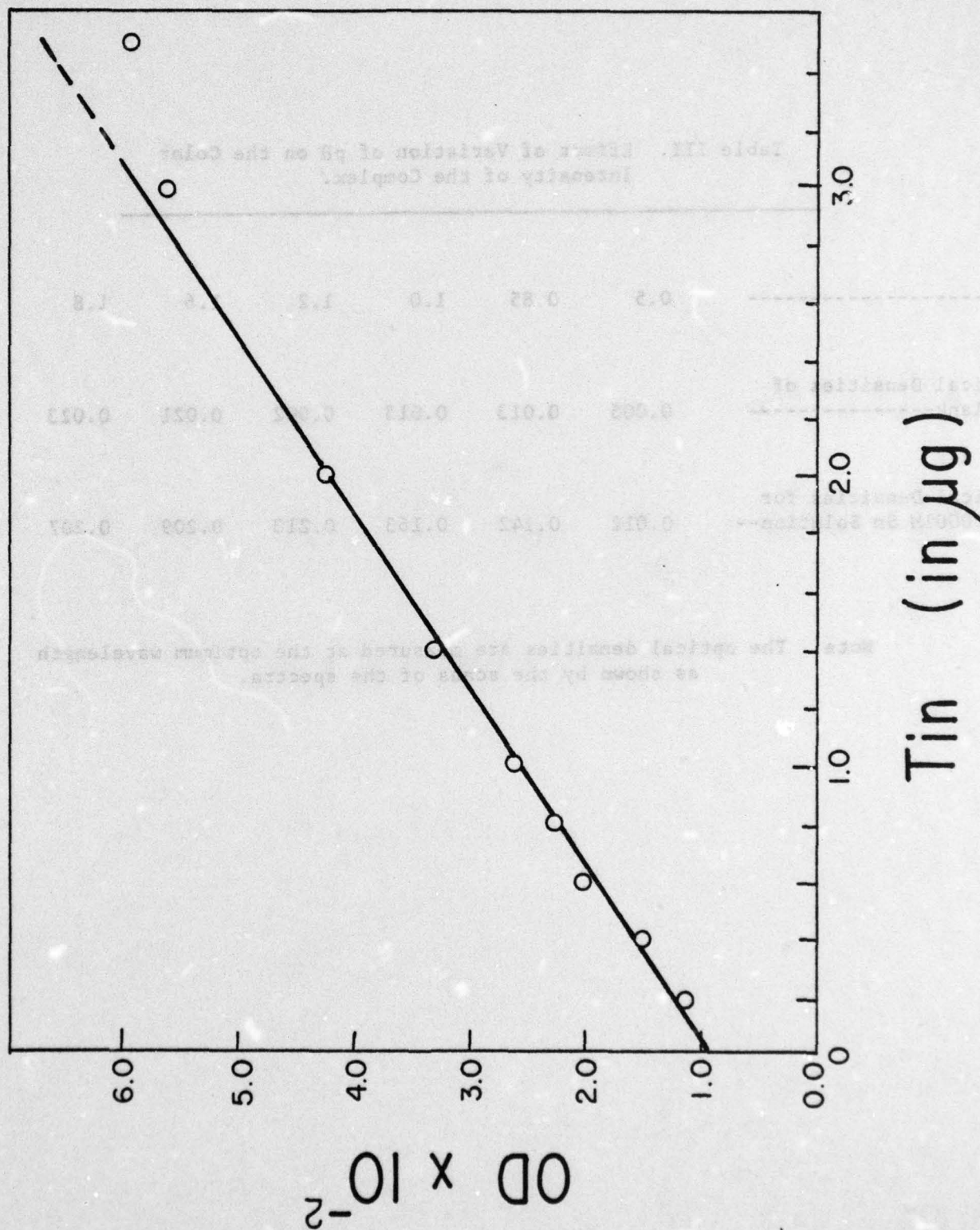


Figure 1b. Least Squares Fits for Calibration Curve.

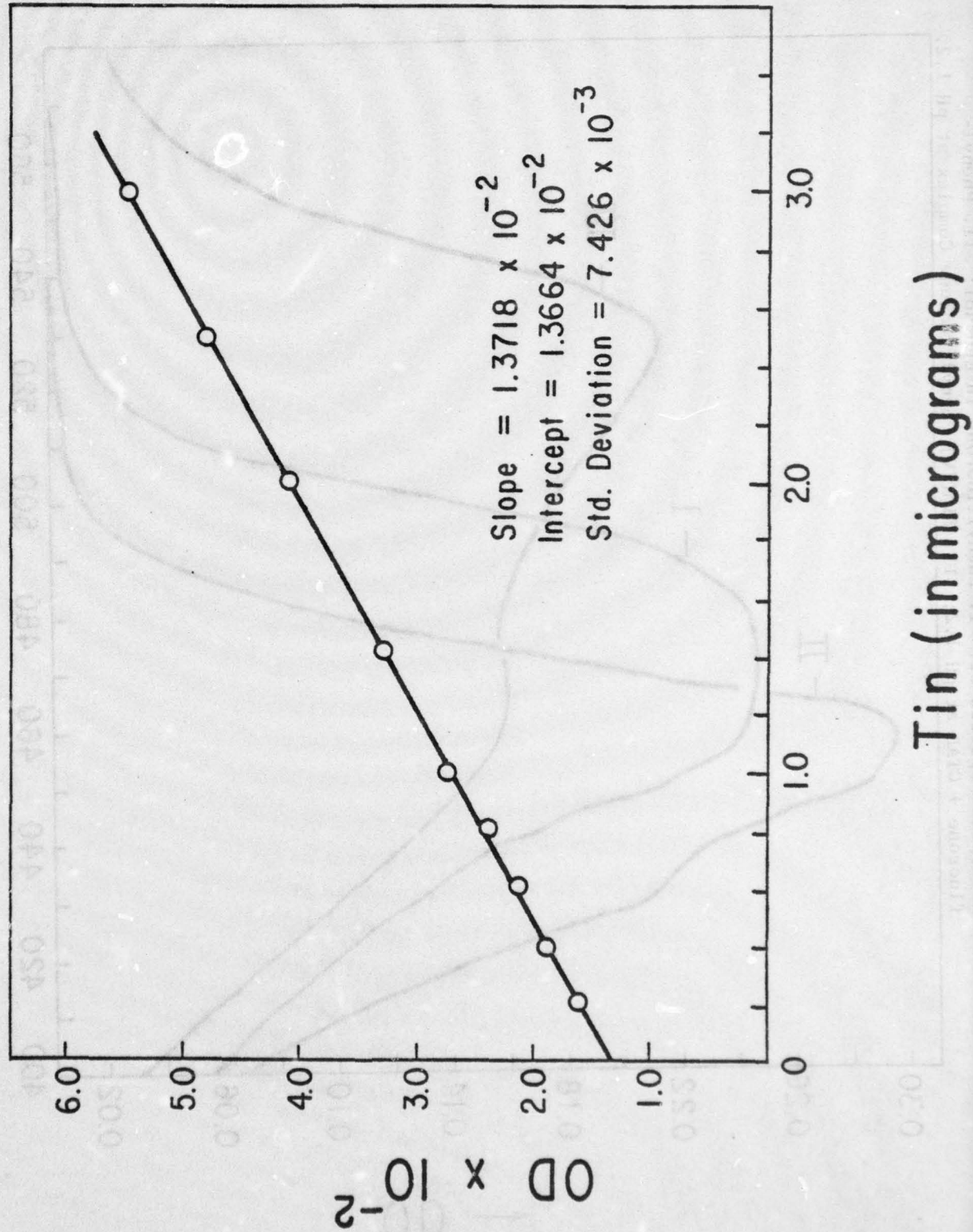


Figure 2. Absorption Spectra of: I. Phenylfluorone in Ethanol; II. Phenylfluorone + CTAB at pH 1.2; III. Tin(IV) Phenylfluorone Complex at pH 1.2.

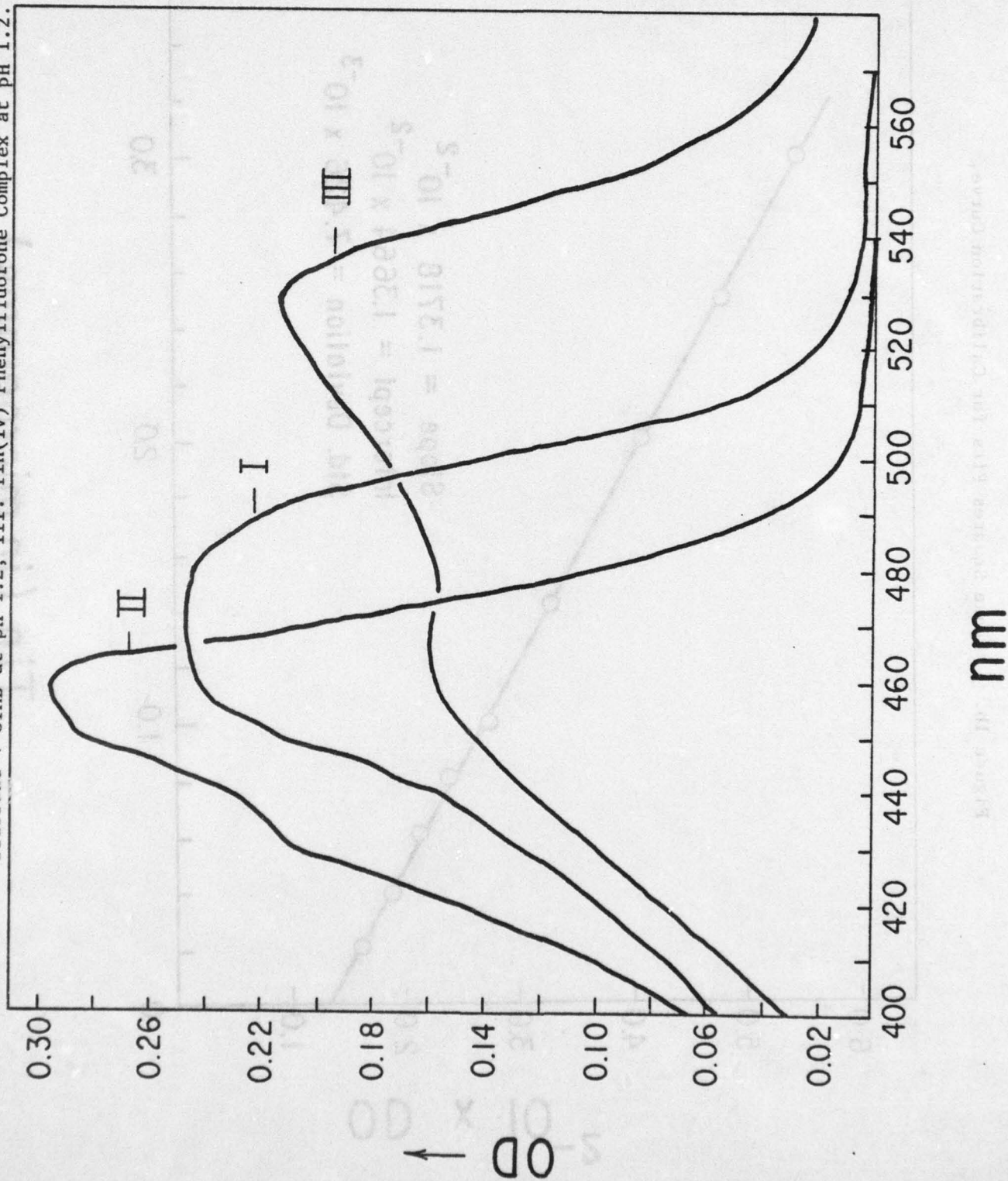
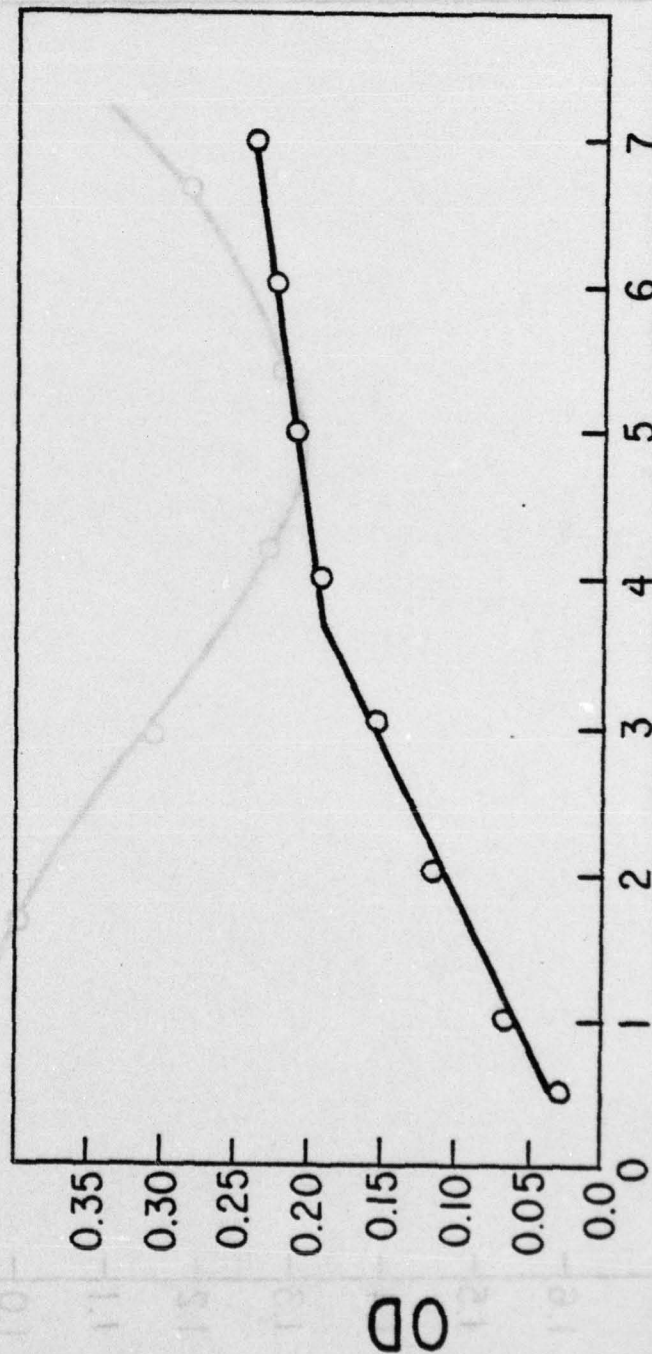
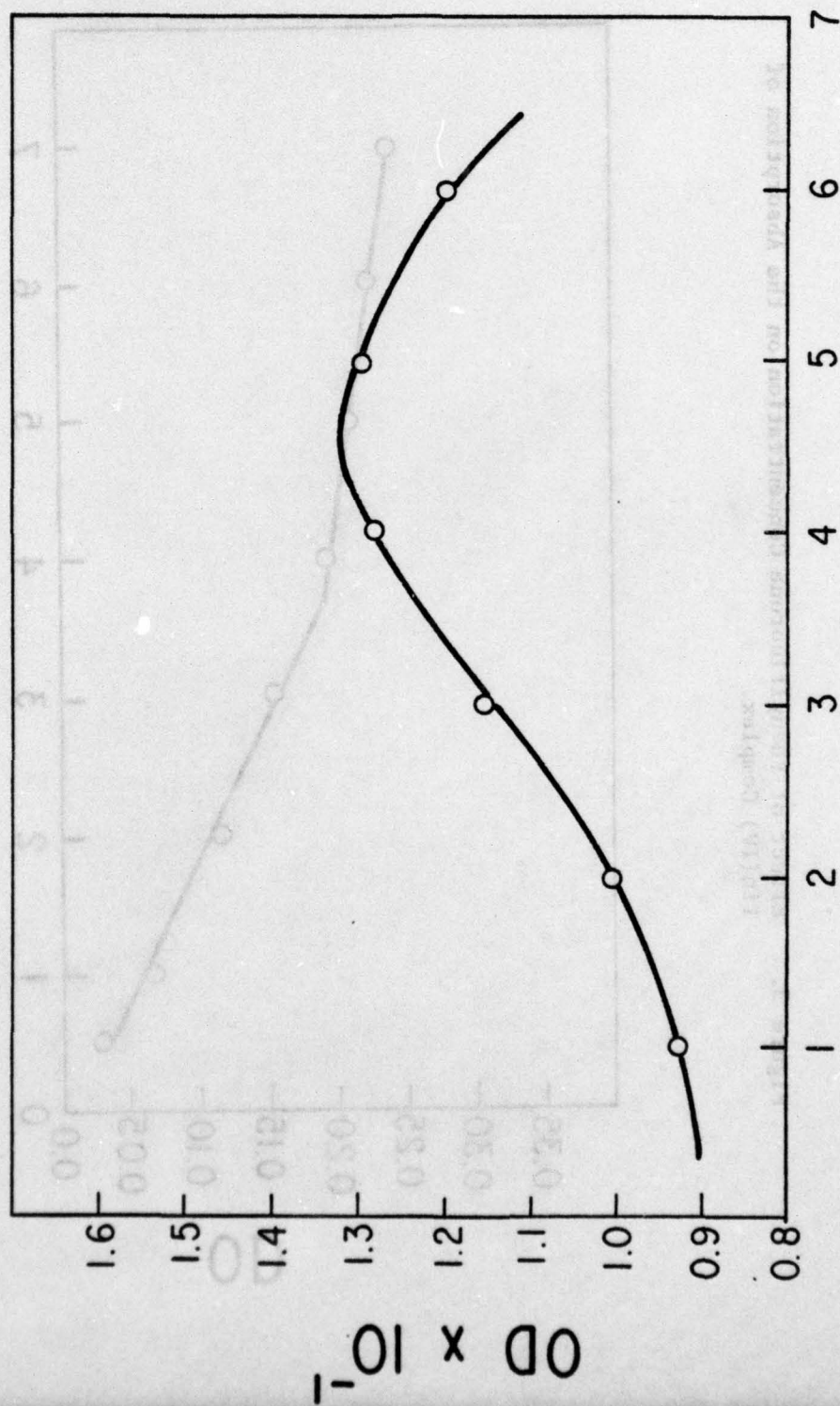


Figure 3. Effect of Phenylfluorone Concentration on the Absorption of Tin(IV) Complex.



Vol. (Flurone)

Figure 4. Effect of CTAB Concentration on the Absorption of Tin(IV) Complex.



Vol. of CTAB

Figure 5. Effect of Time on the Absorption of Tin(IV) Complex.

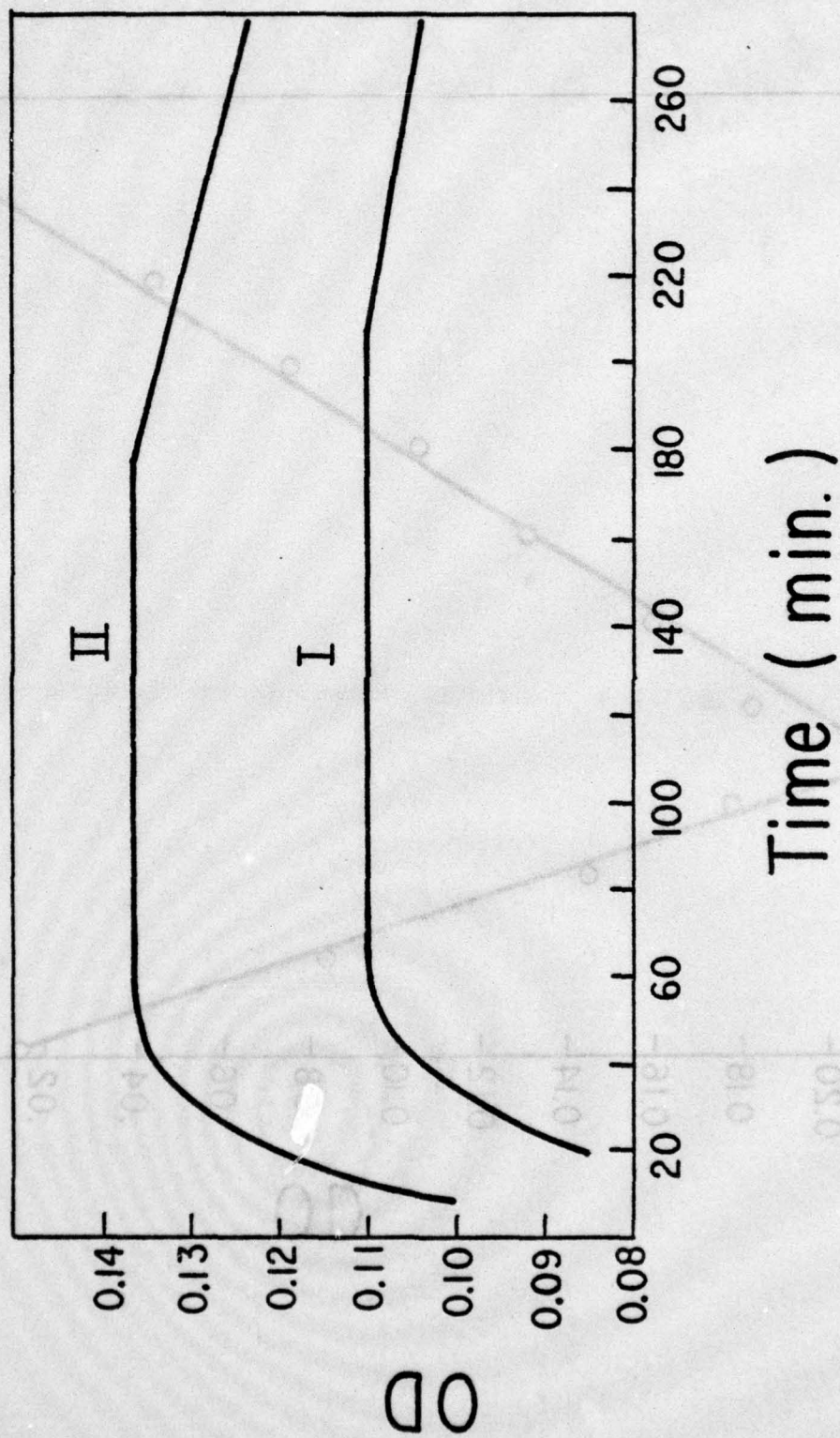
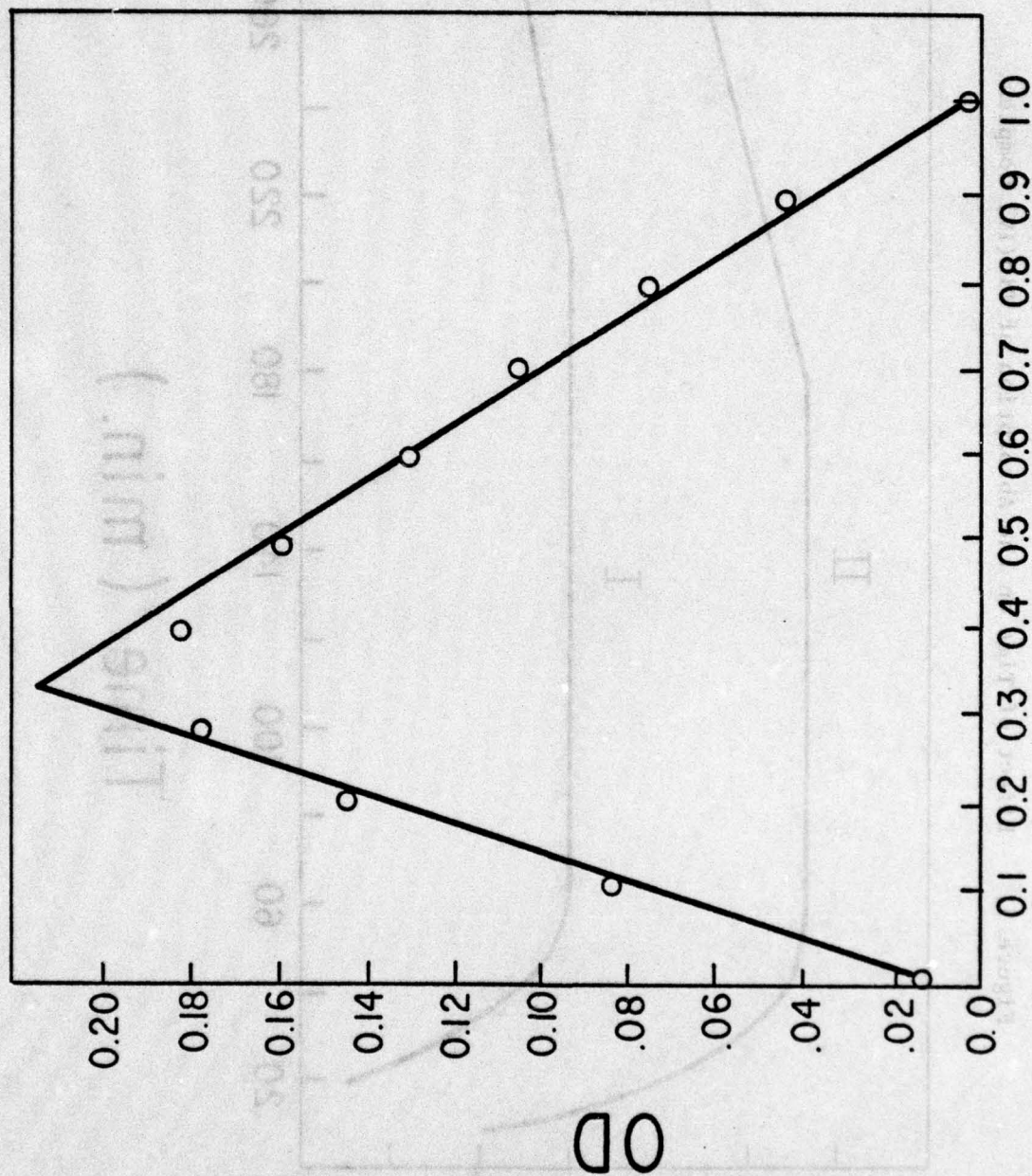


Figure 6. Continuous Variation Method for Tin(IV) Phenylfluorone Complex at pH 1.2.



Mole Fraction ($[Sn]/[Sn] + [Fl]$)

Figure 7a. Mole Ratio Method for Tin(IV) Complex Concentration of Phenylfluorone is Constant.

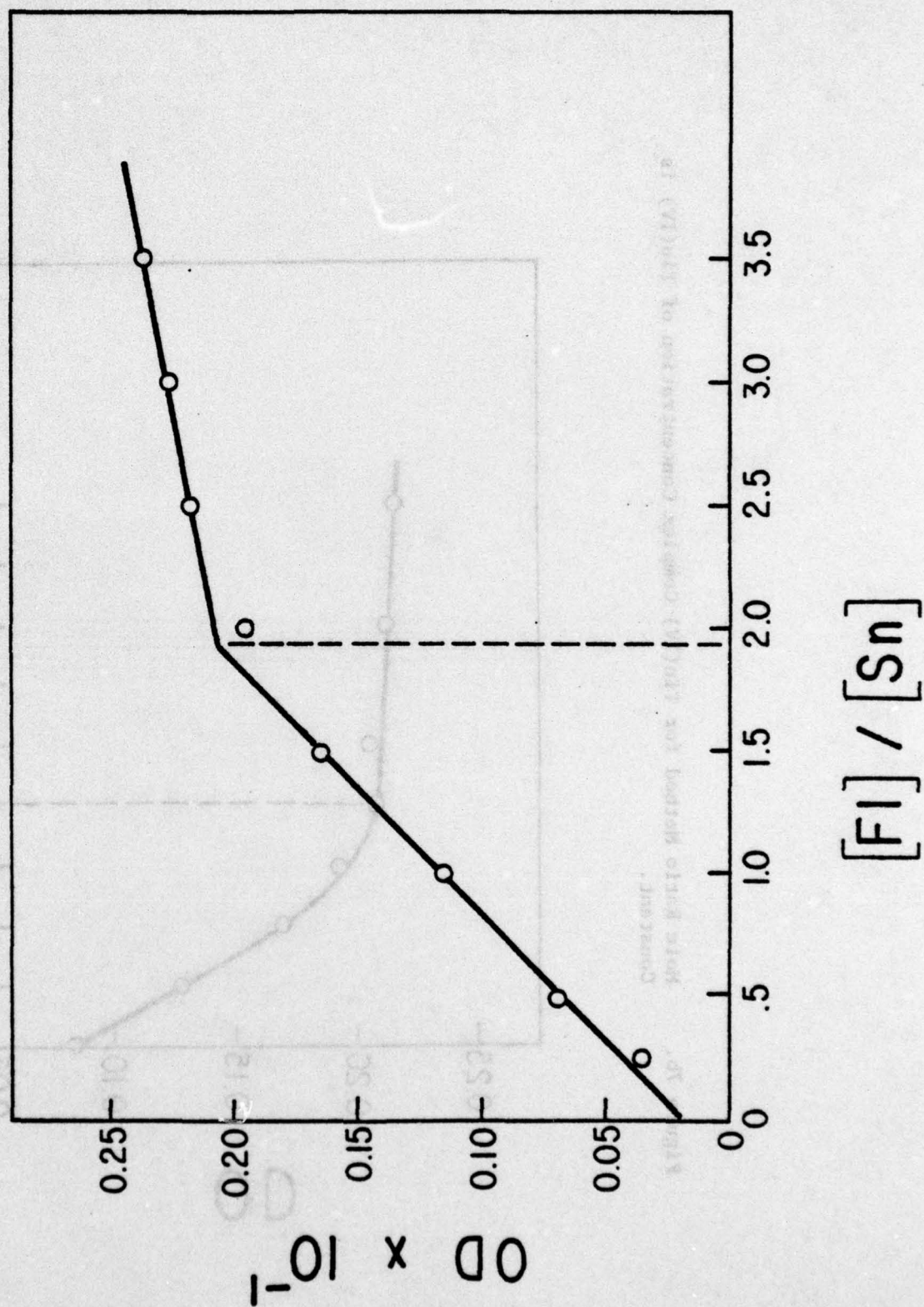
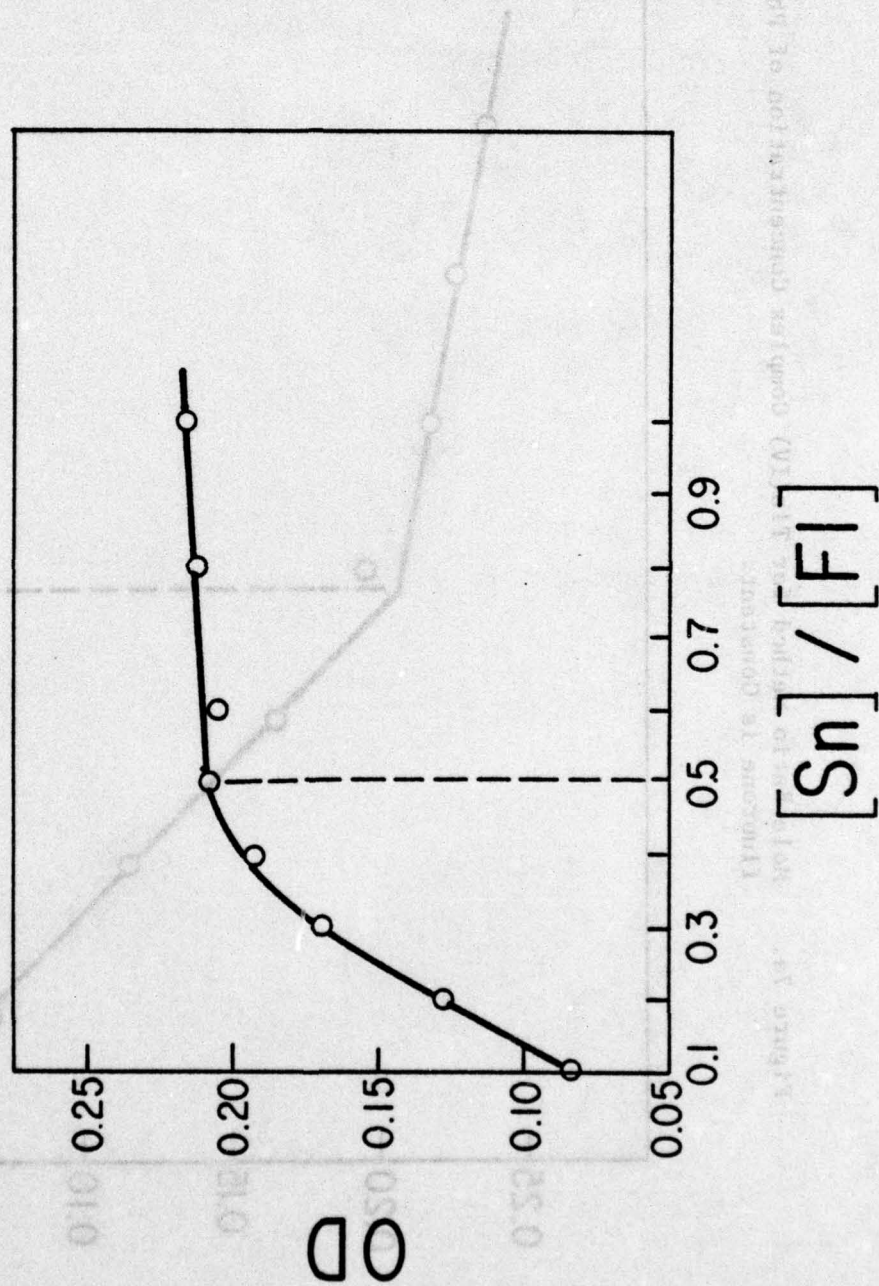


Figure 7b. Mole Ratio Method for Tin(IV) Complex Concentration of Tin(IV) is Constant.



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		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) V. H. Kulkarni and Mary L. Good		8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0836
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of New Orleans Lakefront, New Orleans, LA 70122		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 356-626
11. CONTROLLING OFFICE NAME AND ADDRESS ONR Branch Office 536 South Clark Street Chicago, Illinois 60605		12. REPORT DATE October 20, 1977
		13. NUMBER OF PAGES Nine (9)
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Chemistry Program Material Sciences Division Office of Naval Research, 800 N. Quincy Arlington, VA 22217		15. SECURITY CLASS. (of this report) Unclassified
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18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Phenylfluorone, C.T.A.B., inorganic tin, leaching, seawater		
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